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OPTICAL-PHASE RELAXATION AT LOW TEMPERATURE IN THE LOWEST $^1B_{2u} \leftarrow {}^1A_{1g}$ TRANSITION OF TETRACENE AND PENTACENE IN *p*-TERPHENYL

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Temperature dependent optical absorption experiments on the lowest $^1B_{1u} \leftarrow {}^1A_{1g}$ transition of tetracene in a *p*-terphenyl mixed crystal show that the loss of optical coherence is due to photon emission of the excited state and phonon scattering of the ground state. The resonant phonon that induces the optical phase relaxation process is shown to be of u-symmetry and its lifetime is obtained from the previously reported photon-echo relaxation results. For pentacene in *p*-terphenyl it is concluded that phonon scattering in both the ground and excited state contributes to optical phase relaxation.

1. Introduction

In a previous letter on photon-echo relaxation of tetracene and pentacene in *p*-terphenyl [1] we concluded from the Orbach like echo-relaxation behaviour, that specific resonant phonon modes are responsible for the low-temperature optical phase relaxation process. Proof for this supposition however was lacking and this stimulated us to a further study of these mixed crystals.

In this note we report results of a temperature dependent optical absorption study on tetracene which shows that low frequency resonant phonon modes indeed exist in these mixed crystals. The conclusion is that optical phase relaxation in the purely electronic transition of tetracene at low temperature occurs through the combined effect of loss of a photon in the excited state and scattering of a phonon in the ground state. The phonon scattered is shown to be of u-symmetry and its lifetime is calculated from the photon-echo relaxation results. For pentacene we can only explain the results of the photon-echo and absorption experiments correspondingly by assuming that the frequency of the resonant phonon in the ground and excited state are the same to within the inhomogeneous line-width of the optical transition. Phonon scattering in both the ground and excited state therefore contributes to the loss of optical coherence in this molecule.

Remeasurement of the fluorescence lifetimes of tetracene and pentacene in *p*-terphenyl further shows that the low-temperature photon-echo lifetime is only a factor of two shorter than the fluorescence lifetime. The resulting discrepancy is ascribed to either an experimental artefact or to spectral diffusion within the inhomogeneous absorption line.

2. Experimental

The preparation of the tetracene and pentacene in *p*-terphenyl mixed crystals and the photon-echo setup are described in detail in ref. [1]. Our previous statements on the temperature reading however need some correction. From the reproducibility of further photon-echo measurements we conclude that while the temperature stability of our cryostat is good as 0.01 K, the absolute temperature reading on the crystal is not better than 0.15 K. The cause of this uncertainty is the presence of a temperature gradient in the cryostat which depends on the pressure of the contact helium gas. Since our crystals are much smaller than the temperature probing resistor we end up with the quoted uncertainty in absolute temperature reading.

Finally the optical absorption experiments were recorded with a 3/4 meter 1702 Spex spectrometer equipped with a grating blazed at 5000 Å and 1800 lines per mm.

3. Results

3.1. Hot photon side band

As from our previous photon-echo relaxation measurements on tetracene and pentacene in *p*-terphenyl it was clear that phonons play a dominant role in the optical phase relaxation process, we decided to take a closer look at the phonon side band structure in the absorption spectra of these molecules.

Fig. 1 shows the origin region of the lowest $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of tetracene in *p*-terphenyl at 1.4 and 4.2 K. First note that the doubling of the absorption spectrum is due to the existence of two sites of tetracene in *p*-terphenyl [2]. The spectra show that each origin carries a phonon side-band at 4.2 K which is absent at 1.4 K. This can only be explained if this phonon side band arises from absorption between a thermally populated ground state phonon level and an excited state phonon level of both u-symmetry. The energy of the ground state phonon level may be obtained by monitoring the intensity of the phonon side band in absorption as a function of temperature.

This experiment was done and the results for both

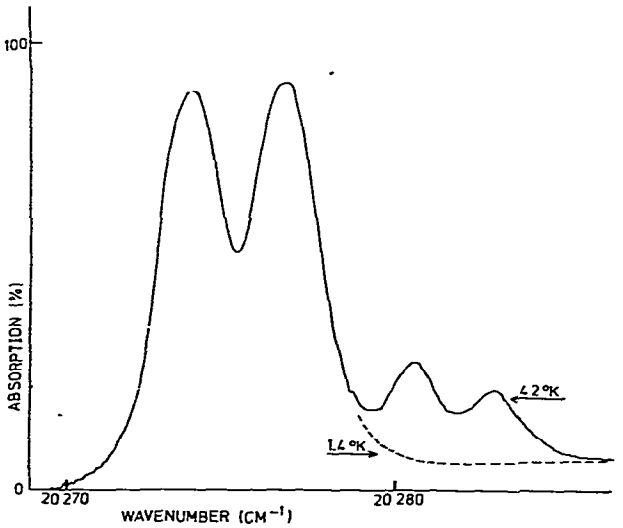

Fig. 1. Origin absorption spectrum of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of tetracene in *p*-terphenyl at 1.4 and 4.2 K. Note that in less concentrated samples the decrease in absorption of the purely electronic transition at 4.2 K is also clearly visible.

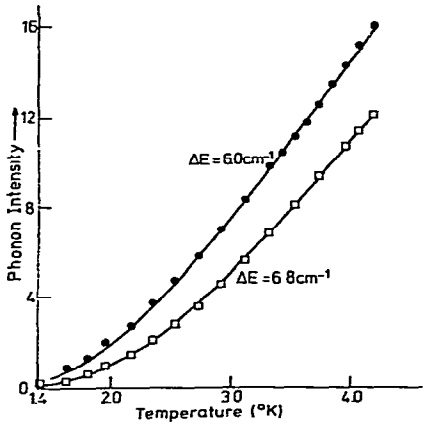

Fig. 2. Graph of the phonon-side band intensity versus temperature. The solid lines are fittings to a two-level Boltzmann population equation with excitation energies as indicated in the figure.

sites are given in fig. 2. The phonon intensities were fitted to the well-known Boltzmann equation for a two-level system

$$I(T) = I(\infty)\,(e^{\Delta E/kT} + 1)^{-1}\,,$$

where ΔE is the ground state phonon energy. From the fittings we calculate ground state phonon frequencies of 6.0 and 6.8 cm^{-1} for the low and high energy site respectively. The corresponding excited state u-phonon frequencies are then obtained by adding the observed spectral splittings and are found to be 12.7 and 13.0 cm^{-1}.

We further note that no other phonon side bands, emanating from the same ground state phonon level, are observed in the absorption spectrum of tetracene.

We finally note that a similar hot phonon side band was not observed in the absorption spectrum of pentacene for temperatures up to 30 K.

3.2. Fluorescence and photon-echo lifetimes

In the course of further photon-echo measurements on dilute mixed crystals of tetracene and pentacene in *p*-terphenyl we found that the fluorescence lifetimes of these samples were much shorter than the ones previously [1] reported. We conclude that the lifetimes reported in ref. [1] are mainly determined by radiation trapping.

We have therefore remeasured these lifetimes (T_{1f}) at 1.4 K and found 19 ± 1 ns for tetracene (35% ab-

sorption) and 24 ± 1 ns for pentacene (10% absorption) in *p*-terphenyl. That these lifetimes are indeed the true fluorescence lifetimes is concluded from the fact that they are identical at the top and in the wings of the absorption lines.

We note here that these fluorescence lifetimes are still a factor of three longer than the ones obtained from gas phase measurements [3].

The photon-echo lifetimes of these dilute samples however were found to be identical to those of the more concentrated samples. This is explained by the fact that absorption of the echo can only lead to spontaneous emission or to secondary echo formation [4]. The echo lifetime thus will be independent of the absorption length of the crystal as long as Beer's law holds for the echo absorption.

4. Discussion

4.1. Photon-echo relaxation model

The level scheme that explains both the phonon side band structure and the photon-echo relaxation behaviour of tetracene in *p*-terphenyl is given in fig. 3. The echo is formed in the transition between the ground (g_1) and pure electronically excited (u_2) state and is relaxed through photon emission and phonon scattering. The decay constants associated with these damping processes may be introduced in a phenomenological way in the density matrix formalism [5]. The off-diagonal elements of the density matrix that control the decay of the echo [4] take the following form:

$$\dot{\rho}_{12} = -\tfrac{1}{2}(\Gamma_{21} + W_{13} + W_{24})\rho_{12} - W_{13}\rho_{11}. \qquad (1)$$

Here Γ_{21} is the fluorescence decay rate constant, W_{13} and W_{24} are the rate constants for the phonon scattering process of the ground and excited state respectively, while the last term accounts for the fact that the trace of the two-level density matrix is temperature dependent. For the interpretation of the photon-echo results below 2.5 K ($kT \ll \Delta E$) this last term can be ignored.

For the photon-echo lifetime ($\frac{1}{2}T_2$) we then find:

$$2/T_2 = (\Gamma_{21} + W_{13} + W_{24}). \qquad (2)$$

Γ_{21} is temperature independent and W_{13} and W_{24} are assumed to be related to the phonon lifetimes in the following way: e.g. $W_{13} = \tau_3^{-1}\, e^{-\Delta E/kT}$. Here τ_3 is the phonon lifetime and ΔE its energy. For tetracene the excited state phonon frequency is about twice as large as that of the ground state and in this case the approximation $W_{24} \ll W_{13}$ for temperatures below 2.5 K seems warranted. With these assumptions we find for the photon-echo phase-relaxation time T_2 for tetracene:

$$T_2^{-1} = \tfrac{1}{2}(\Gamma_{21} + W_{13}) = 1/2T_{1f} + (1/2\tau)\, e^{-\Delta E/kT}. \qquad (3)$$

In our previous letter on photon-echo relaxation of tetracene [1] such a temperature dependence of the echo relaxation rate indeed was reported and an energy gap (ΔE) of 8.1 ± 1 cm^{-1} was obtained for the high energy site. From the temperature dependence of the phonon side band in absorption we find ΔE = 6.8 ± 0.7 cm^{-1} for this site. We therefore conclude that the temperature dependence of the photon-echo intensity is due to scattering of the ground state to a local phonon state. We further calculate from the pre-exponential factor in the echo relaxation behaviour that the lifetime of this phonon state is 40 ps. The similar temperature dependence of the photon-echo relaxation in pentacene suggests that the same model holds for its explanation.

The absence of a hot phonon side band must be explained then be assuming that the ground and excited state phonon frequency are, to within the inhomogeneous optical linewidth, the same (ca. 21 cm^{-1}). The phonon lifetime in ground and excited state is then calculated to be 22 ps.

We further note that eq. (2) shows that at low temperature the photon-echo lifetime is expected to con-

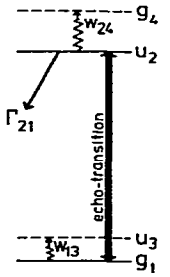

Fig. 3. Low-temperature photon-echo relaxation model for tetracene and pentacene in *p*-terphenyl. The dashed lines indicate phonon levels and the symmetry symbols refer to the total symmetry of the state (electronic ⊗ phononic). Note that the phonon side-bands in fig. 1 arise from the $g_4 \leftarrow u_3$ transition in tetracene.

verge to the fluorescence lifetime. The low-temperature photon-echo decay times for both tetracene and pentacene however are still found to be a factor of two shorter. Spectral diffusion within the inhomogeneous absorption line may be responsible for the discrepancy. At present however we are not able to exclude an experimental artefact in the sense that the laser beam divergence is not constant when, during an echo-lifetime measurement, the delay between the exciting pulses is increased. This is a point of further investigation.

4.2. The nature of the phonon state

From the photon-echo results on tetracene and pentacene in *p*-terphenyl mixed crystals we conclude that the phonon states, that induce optical phase relaxation, are strongly dependent on the guest molecule. We therefore suggest that these phonons correspond to resonant phonon modes [6,7]. This type of phonon mode is characterized by a narrow linewidth and a large amplitude at the guest site and is therefore eminently suitable to relax the optical excitation. Further experiments to clarify the nature of these phonon state however remain highly desirable. We suggest e.g. far infrared experiments to be done on these mixed crystals. Such experiments might also expose the hereto hidden resonant phonon-mode in the pentacene mixed crystal.

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